

XAFS speciation of adsorbed zinc ion on allophane in presence of humic acid

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Introduction

Humic acid (HA), which is one of the humic substances, is widely present in natural soils. HA influences the adsorption of heavy metal ion on soil [1]. Thus, it is important to evaluate the contribution of HA to the adsorption of heavy metal to the soil for environmental assessment.

We investigated the quantity of adsorbed zinc ion on soil in the condition containing HA. Amorphous clay mineral "allophane" was used as modelled soil. In our previous work, the quantity of adsorbed zinc ion on allophane decreased as the concentration of HA increased at pH7. It is known that pH influences the quantity of metal ion adsorption. Though all samples had same pH, the quantity of adsorbed zinc ion on allophane was different by influence of HA. To investigate the difference of the quantity of adsorbed zinc ion on allophane from adsorption structure, we analyzed zinc ion adsorbed on allophane by XAFS measurement.

Experimental

Allophane was prepared in reference to coprecipitation method [2]. HA was supplied by Wako pure chemical industries. The commercial HA was purified by 1M NaOH and 3M HCl. 5 ml of 5×10^{-3} M zinc chloride solution and 5 ml of HA solution (0, 2, 20, 40 ppm, respectively) were added to 0.1 g of allophane powder and the mixed solutions were stirred at room temperature for 24 hours. After the reaction, the samples were filtered by 0.45 μ m pore size membrane filter (Millipore, HAWPO 4700) and separated to the liquid and the solid phase. The quantity of adsorbed zinc ion on allophane was calculated from the difference of the liquid phase concentration of zinc before and after the reaction. Then, the solid phase was measured by XAFS. All solid samples were washed by deionized water three times to remove zinc ion remaining among the particles. The wet solid samples were immediately put into a polyethylene film and sealed. Beam line was used at BL-12C, and the spectra were collected in fluorescence mode using a Lytle detector at room temperature.

Results and Discussion

Zinc K-edge XANES spectra of allophane adsorbing zinc ion are shown in Fig.1. Only the spectrum (e) of the sample which zinc ion adsorbed on HA itself has relatively sharp peak. To elucidate which would have larger contribution to the zinc adsorption between allophane and HA, contribution ratio was determined by pattern fitting using the normalized spectra of Zn-

allophane (a) and Zn-HA (e) shown in Fig.1. As a result, almost all of zinc ion was adsorbed on the surface of allophane. This result implies that HA hardly participates in adsorption of zinc ion. In general, HA and allophane have high affinity. We presumed that HA was combined with allophane and then adsorption sites of allophane were decreased. This means that HA adsorbed on the surface of allophane disturbed adsorption of zinc ion by steric barrier. We consider that these facts are the reasons why the quantity of adsorbed zinc decreased as concentration of HA increased (Fig.2).

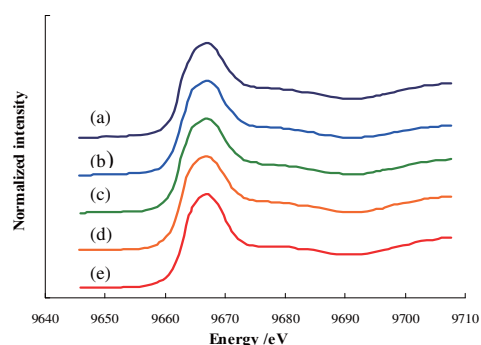


Fig.1. Zinc K-edge XANES spectra of allophane adsorbing zinc ion. (a):allophane only, (b):HA 2 ppm, (c):HA 20 ppm, (d):HA 40 ppm, (e):HA only. All spectra were normalized based on white line.

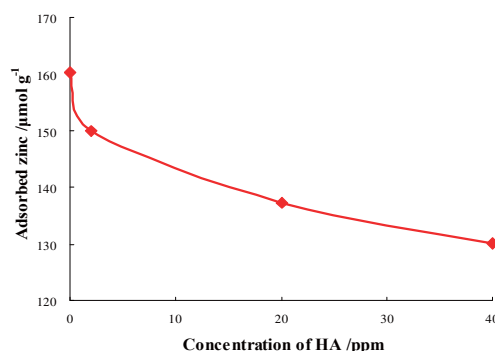


Fig.2. The quantity of adsorbed zinc on 1 g of allophane under the condition of HA concentration 0, 2, 20, 40 ppm.

References

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